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Application of Library Design and Calibration to a Real Problem

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NCMC-1: Library Design and Calibration

April 26th, 2002

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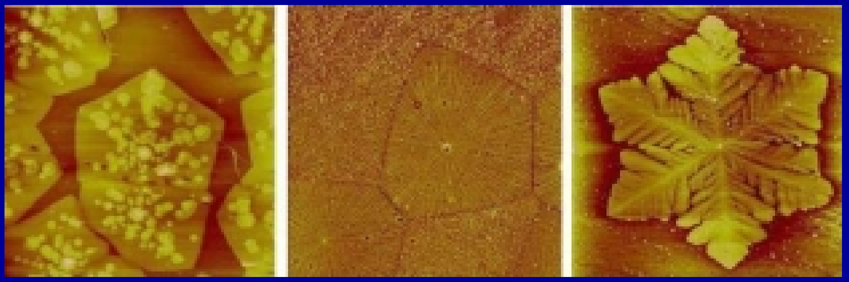
Combinatorial Methods at NIST

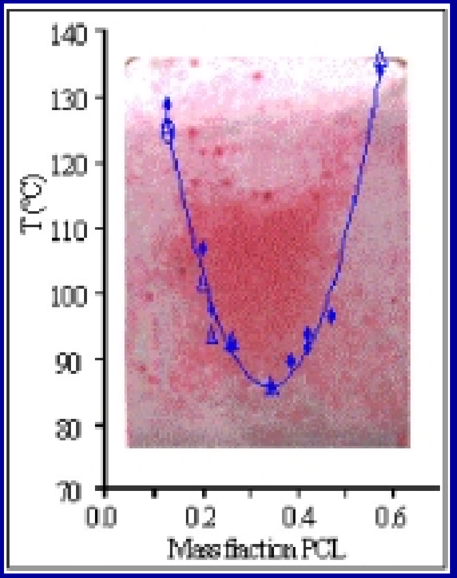
Polymers

- Block Copolymers
- Adhesion
- Formulations
- Crystallization
- Fire Retardants (BFRL)



Biomaterials

- Biocompatibility
- Bio-adhesion
- Cell Growth
- Patterned Activity
- Recognition



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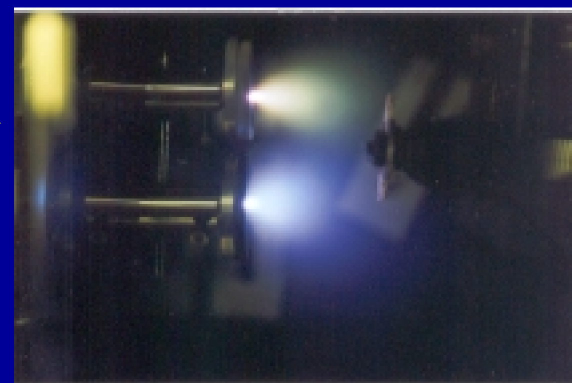
Combinatorial Methods at NIST

Metals and Alloys

- Dielectric Oxide Films
- Semiconductors

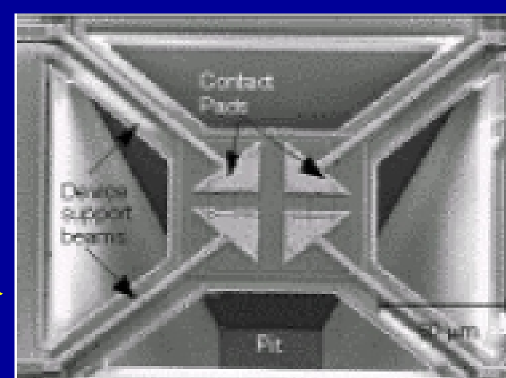


Chemical Analysis

- Chemical Microscopy by SIMS
- High-throughput IR Imaging

Thermal Properties

- Service Life Prediction
- Micro-hotplate Arrays



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Review of Gradient Library Procedure

Design

1. Define problem / parameter space
2. Survey existing techniques
3. Develop and evaluate
4. Refine the method
5. Extend the method

Calibration

1. Defect analysis
2. Set up spatial reference grid
   - Mesh of calibration measurements
3. Determine library errors
   - Resolution
   - Tolerance
   - Uncertainty
4. Combinatorial measurements
5. Refine the procedure

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Design

Definition of problem
- Block copolymer thin film behavior

Initial gradient library
- Film thickness gradient

Adding an orthogonal library
- Thickness and surface energy

Exploring three dimensions
- Thickness and temperature and time

Calibration

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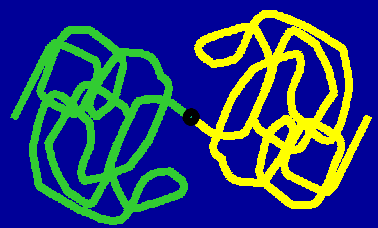
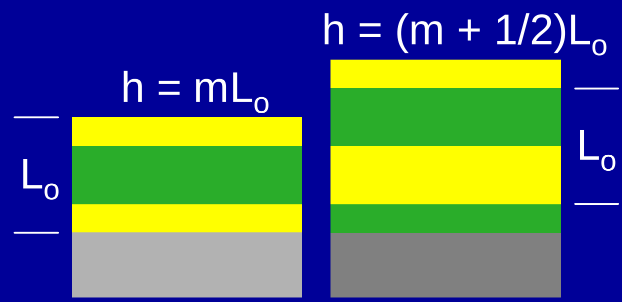
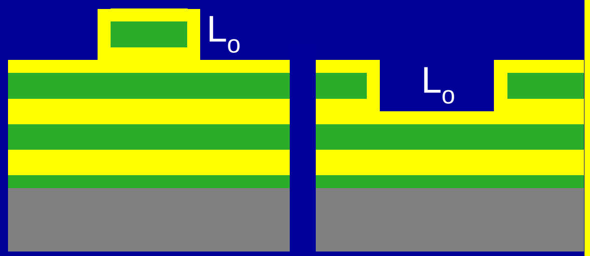
Define Problem / Parameter Space

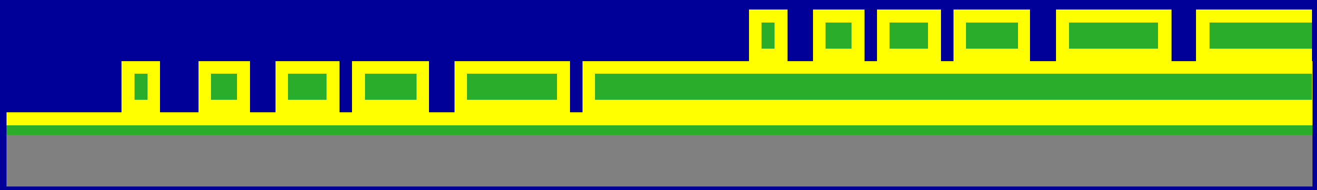
Block copolymer thin film morphology







Two polymers joined together form lamellae that lay parallel to the substrate
For certain film thickness, complete lamella form and the surface is smooth
Otherwise incomplete lamella form and the surface is not smooth



Want to cast thickness gradient to study morphology of these films
Thickness range ≈ 40 – 120 nm

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Fabricate Library and Evaluate

Thickness gradient range lends itself to flow coater

1st attempt:

PS-b-PMMA in toluene

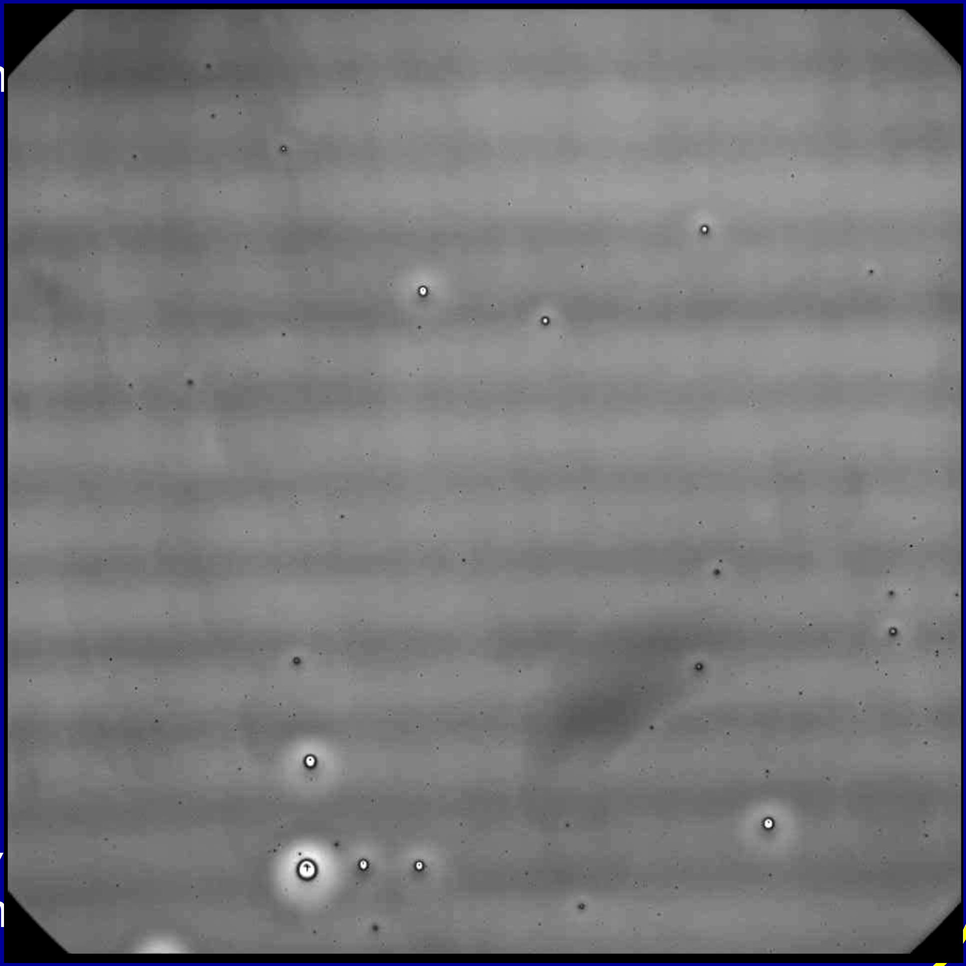
Result:

Gradient produced but horizontal stripes are thickness variations

Diagnosis:

Toluene isn't an optimal solvent for both blocks, need to find a better solvent

40 n



80 n

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Refine Library Development

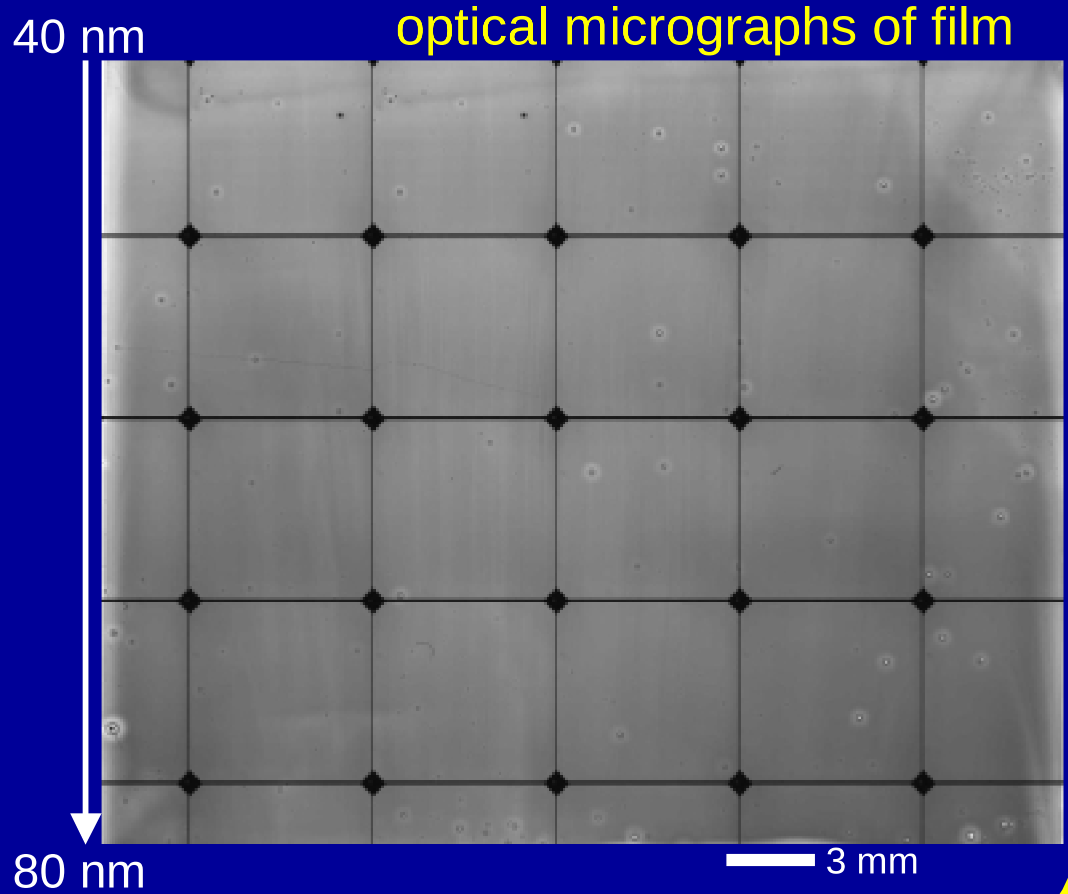
Now test different solvents to find one to produce smooth gradients

Determine a 50/50 mixture of toluene and chloroform give optimal combination of defect free film and gradient slope

2^{nd} attempt:

Film produced without line thickness defects

optical micrographs of film



Library Calibration: Standard Reference Grids

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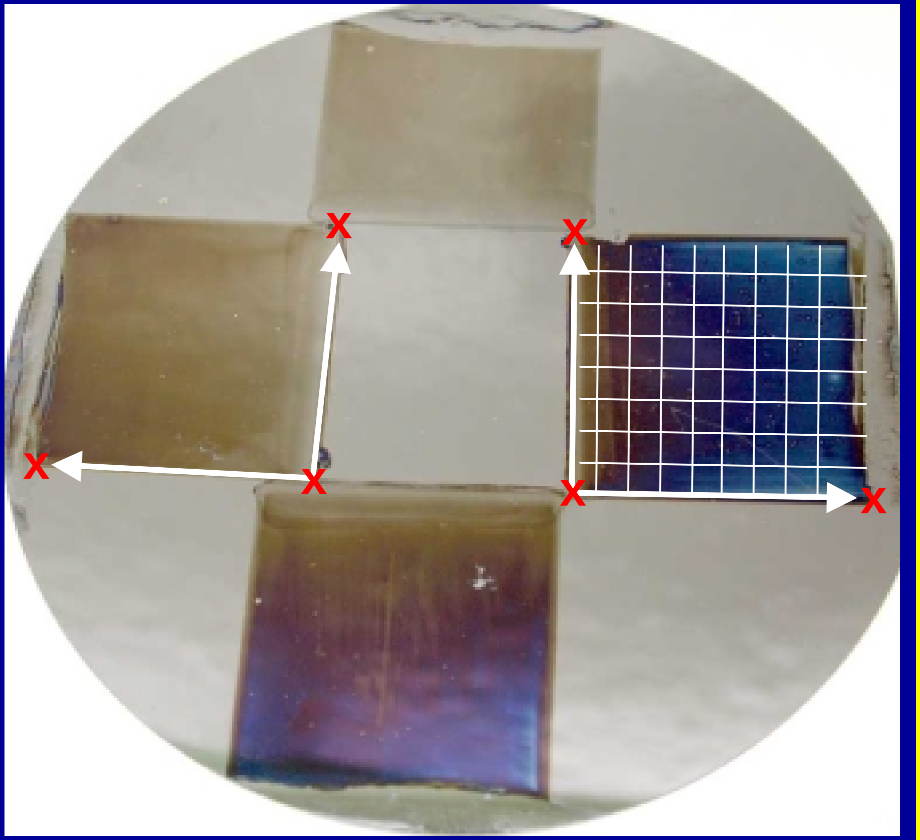
Select the library corners as fiduciary marks (x)

Define a coordinate system and spatial reference grid (SRG) for each set of fiduciaries



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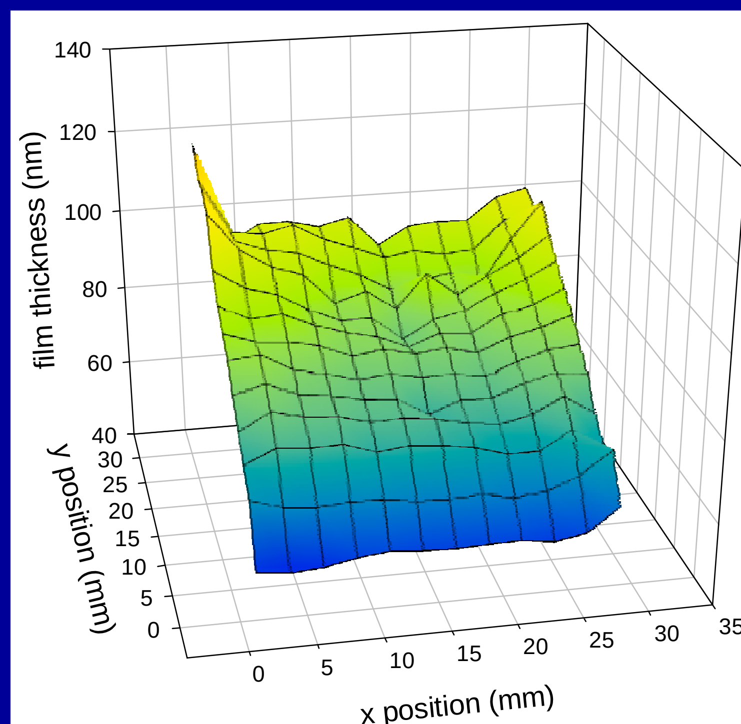
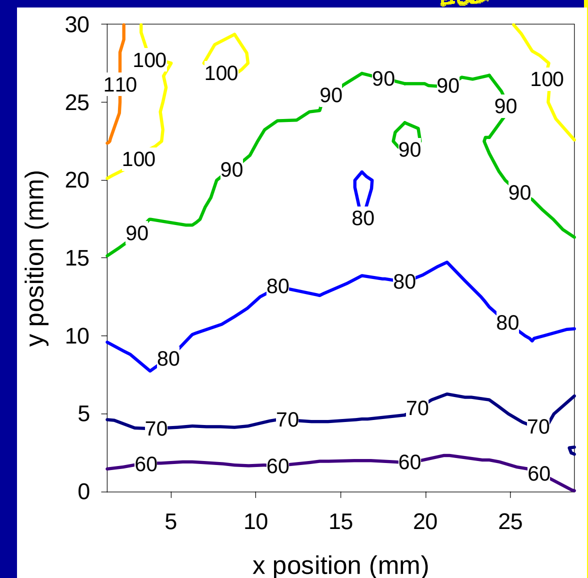
Library Calibration: Thickness Determination

Gradients are generally non-linear, need to determine thickness

Use SRG to measure the film thickness





Convert grid measurements into a thickness contour map

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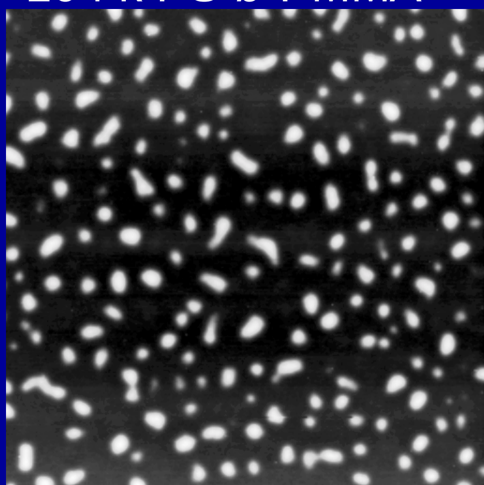
Library Calibration: Experimental Resolution

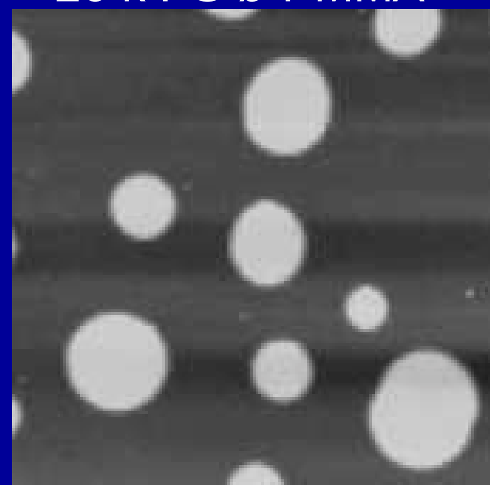
Atomic Force Micrographs of surface islands

104 k PS-*b*-PMMA



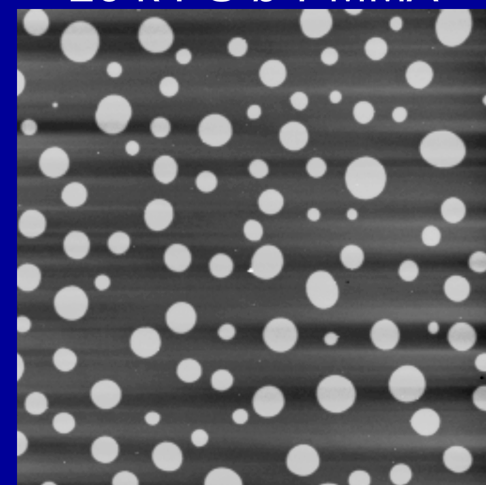
4 μm

26 k PS-*b*-PMMA



4 μm

26 k PS-*b*-PMMA



10 μm

High M_w features are ~ 1 μm so a 20 μm scan yields sufficient features

When M_w is decreased a 20 μm scan yields < 10 islands

Increase scan size to 50 μm to increase statistics to sufficient levels

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Library Calibration
Thickness Gradient Morphology

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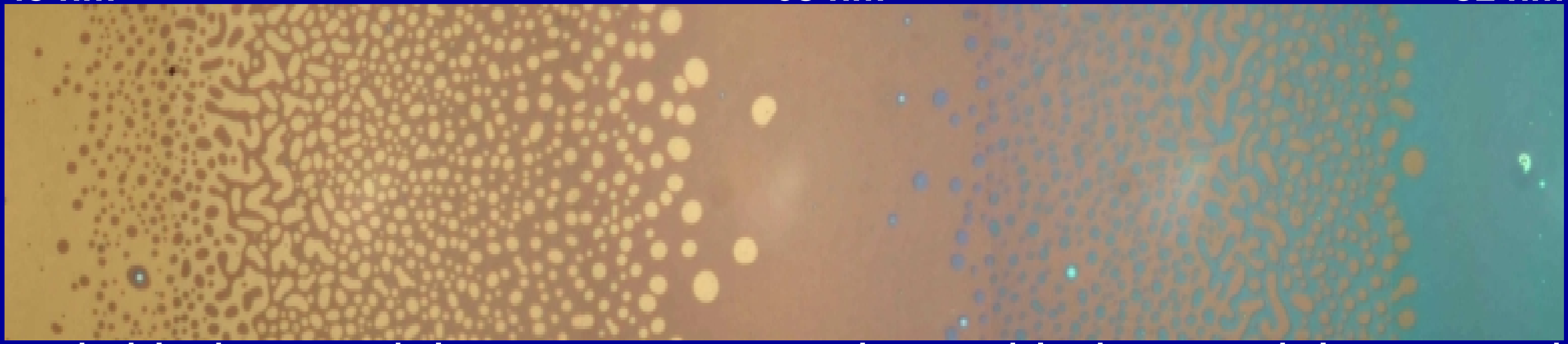
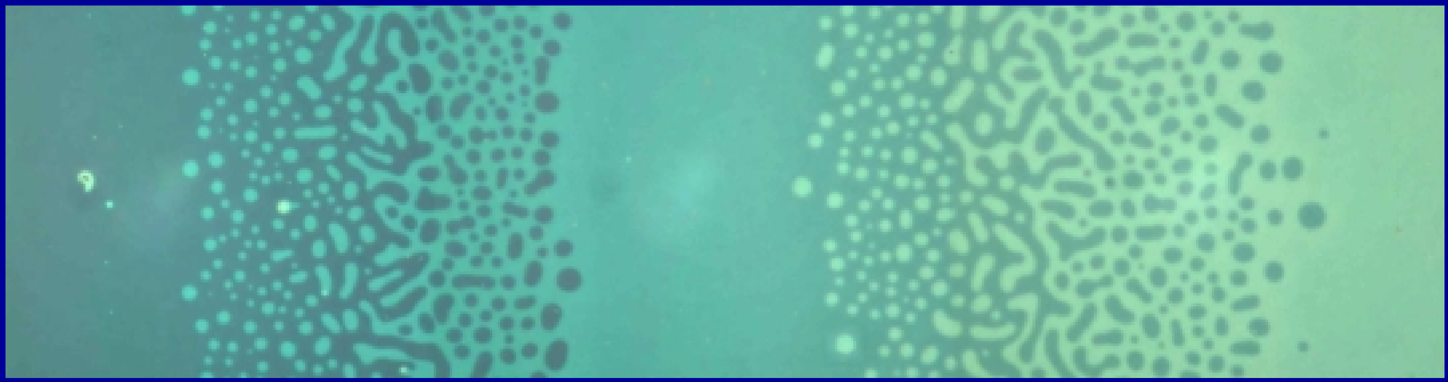
Optical Micrographs of 26k PS-b-PMMA, annealed 6 h





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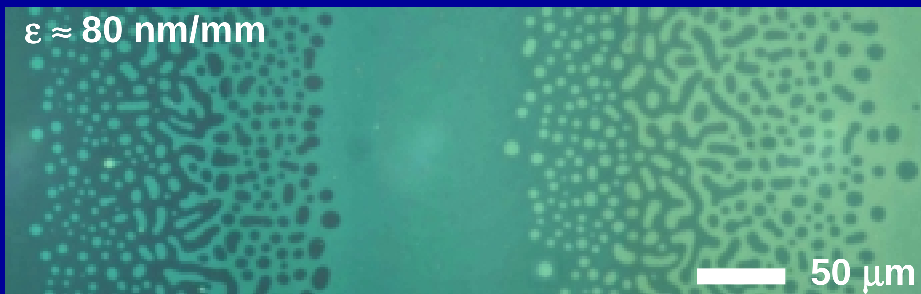
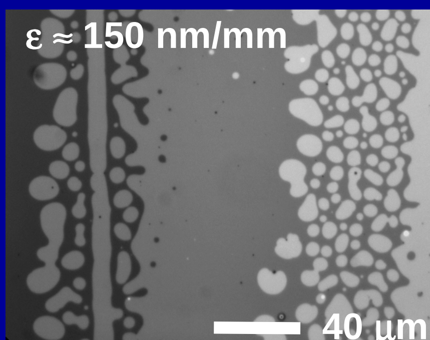
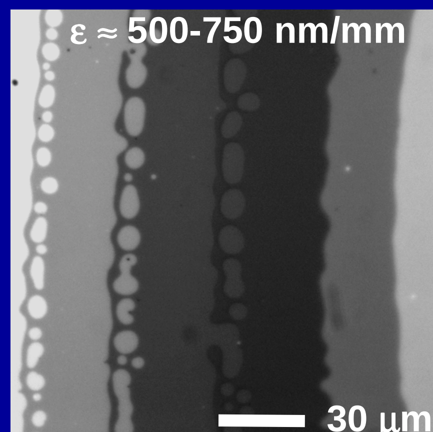
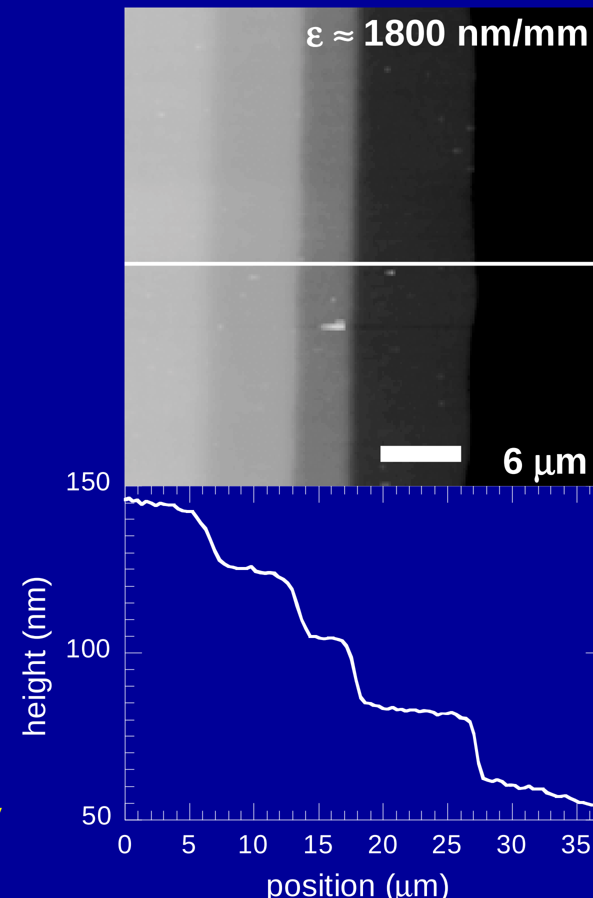
Library Calibration
Effect of Gradient on Morphology









Increasing gradients induce change in morphology
Typical flow coater gradients ~ 0.5 - 2 nm/mm

Although this example is beyond normal experimental range, demonstrates possibility for gradients effecting phenomena

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Definition of problem

Block copolymer thin film behavior

Initial gradient library

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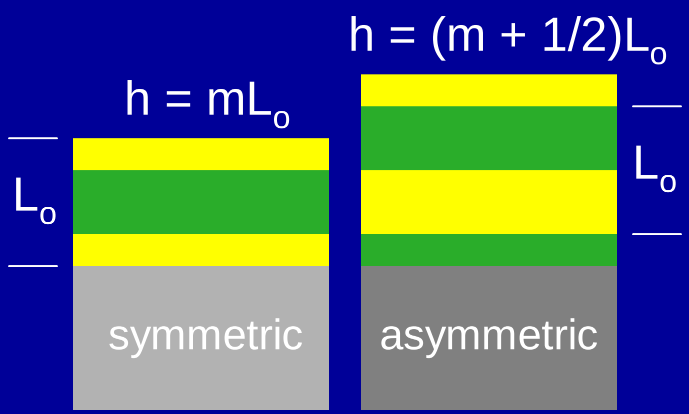
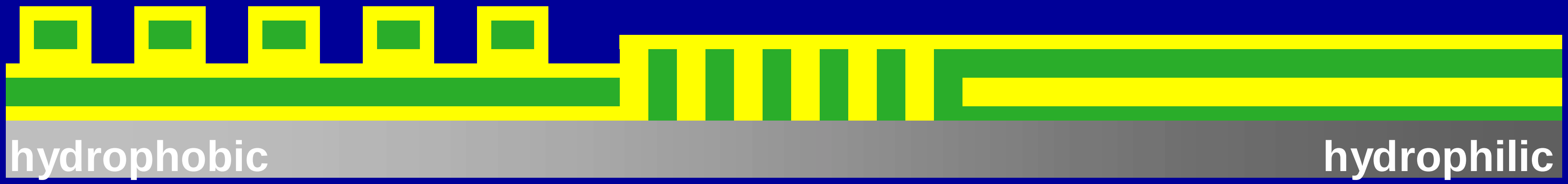
Increase Complexity: Adding a Second Gradient

Known that changing substrate energy can modify which block is near the substrate



Use substrate energy gradient orthogonal to a film thickness gradient to investigate this more thoroughly



Surface Energy Gradient: Creation

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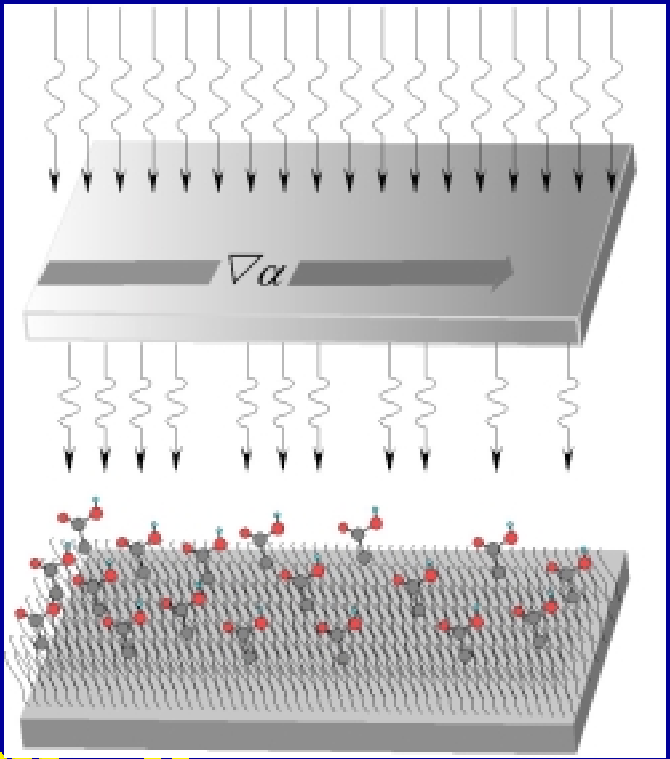
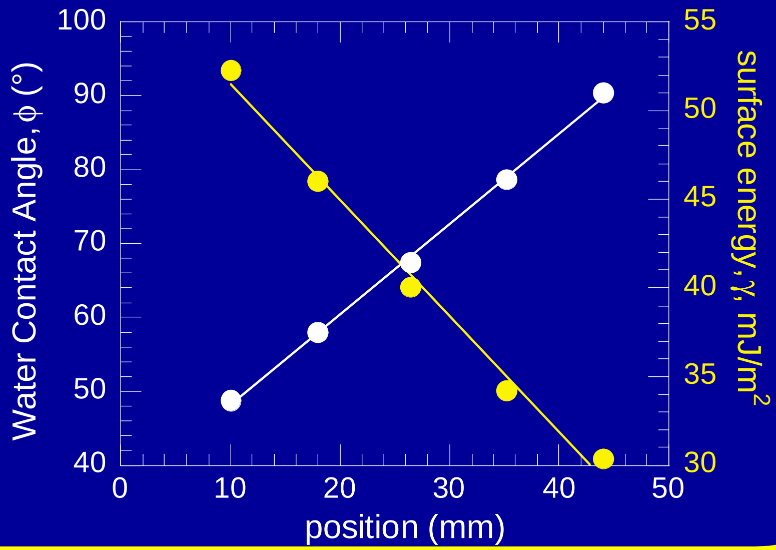
Create silane self-assembled monolayer on a clean Si surface

Expose SAM to UV radiation through a fused silica gradient filter



UV exposure produces a moiety gradient across the surface resulting in a surface energy gradient



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Surface Energy Gradient Sample

26k PS-b-PMMA annealed 64 hr at 170°C

~ 120 nm

h

~ 60 nm

γ

surface
patterns

smooth
regions

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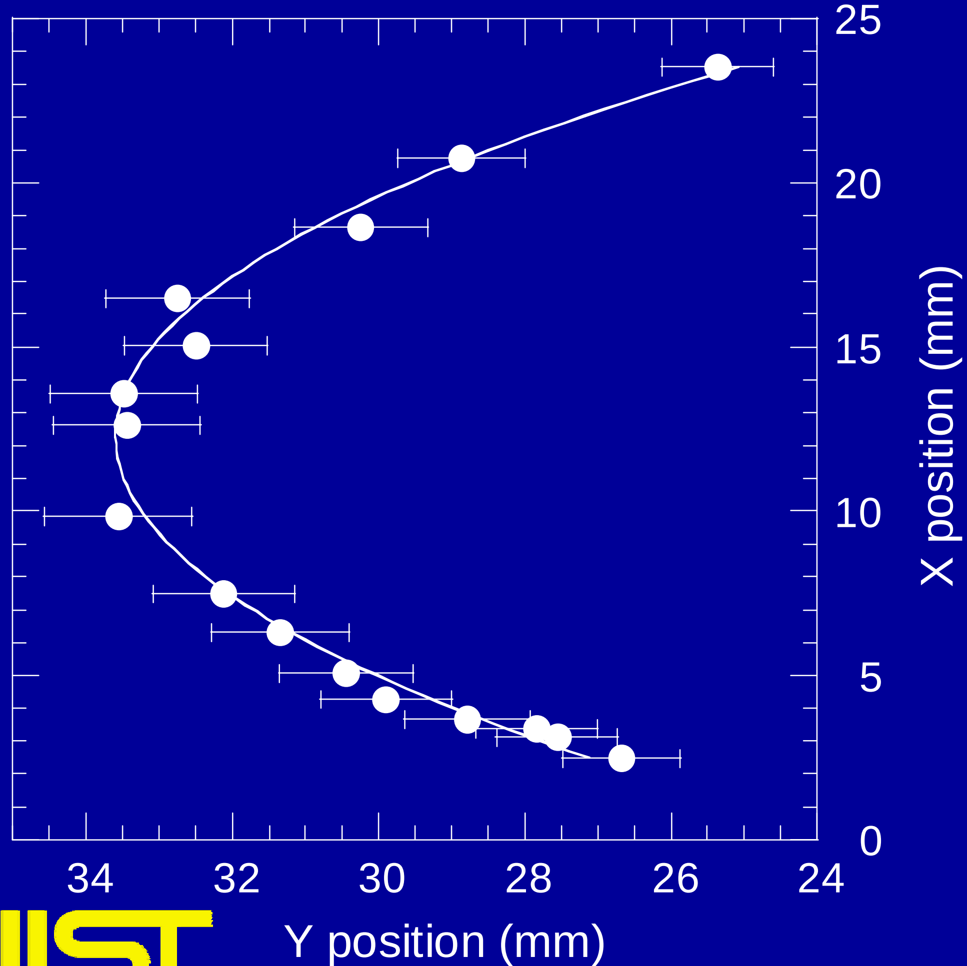
Neutral Point Location

Neutral point tracks γ = ~38 mJ/m^2 across the sample.



Indicative of a non-monotonic dependence of surface energy

Attributed to non-uniform diffusion of ozone between the UV-gradient filter and the substrate

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Refine Technique:
Surface Energy Gradient

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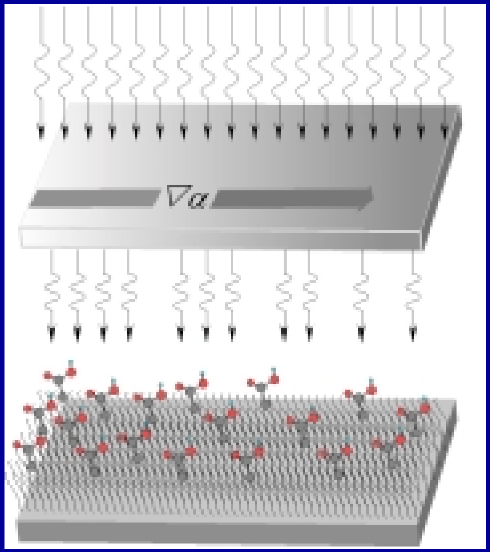
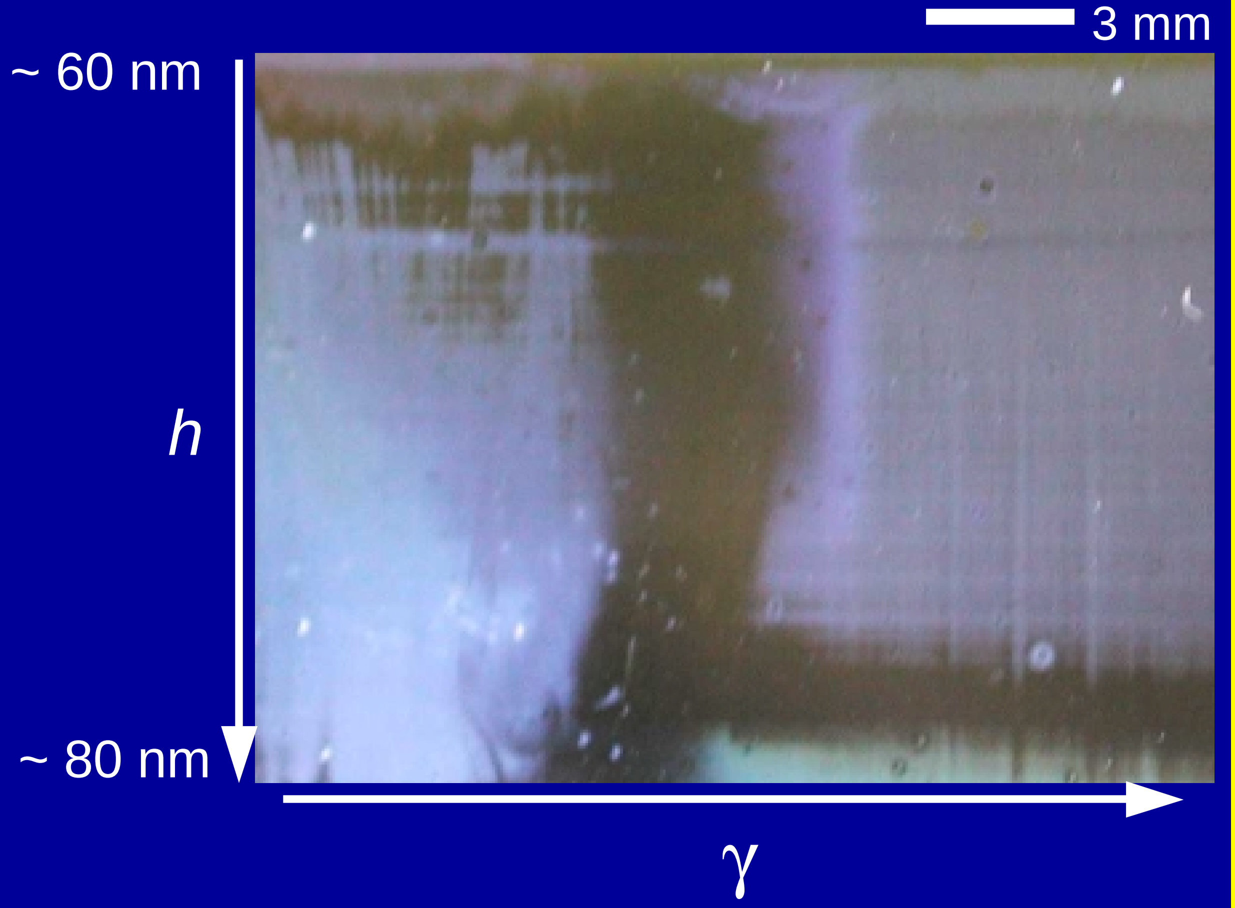
Modification:

Increase diffusion uniformity by increasing the distance between the UV gradient and the substrate





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New Technique:
Surface Energy Gradient

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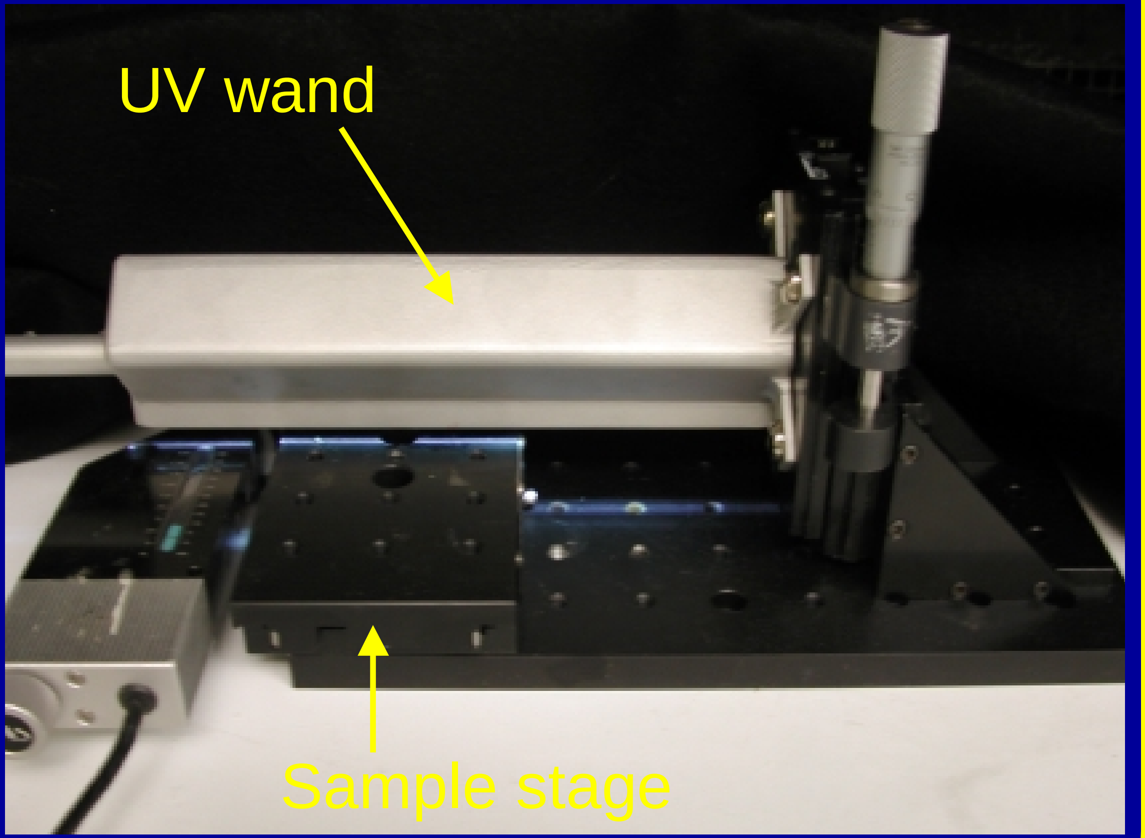
New Design:

Instead of using a UV filter, can vary the UV exposure by moving a UV wand over the substrate at variable velocity

This eliminates the diffusion problem entirely



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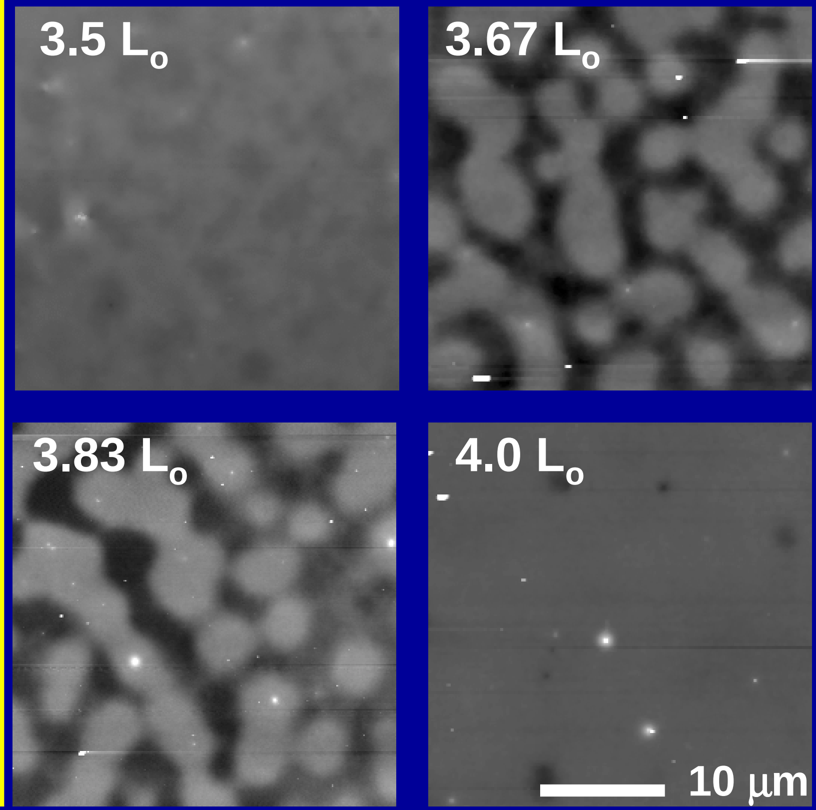
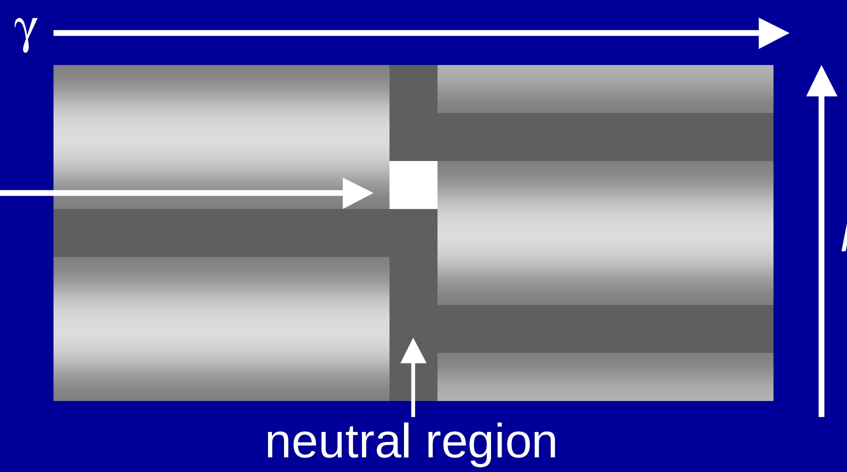
Library Calibration: Effect of Surface Energy Gradient Slope

AFM micrographs at neutral point, SHOULD BE SMOOTH





Hypothesize surface patterns propagate across the neutral region due to their proximity

Neutral region width ≈ 1 mm

Decrease slope to increase separation

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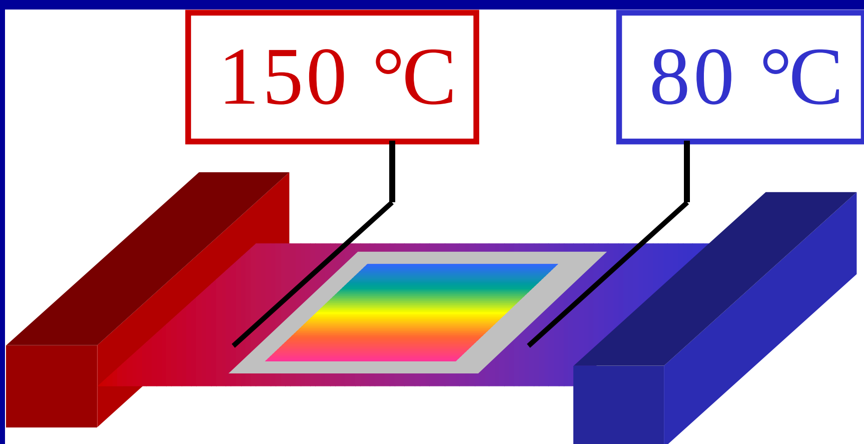
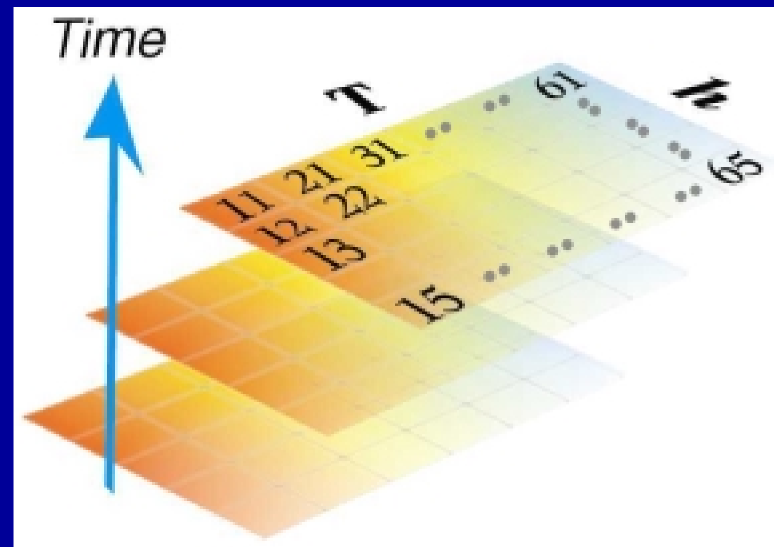
Increasing Complexity: Three Dimensions

Investigate kinetics of surface patterns as a function of film thickness and annealing temperature



Use film thickness gradient orthogonal to temperature gradient



Acquire optical micrographs at time intervals to investigate the evolution of the film surface morphology

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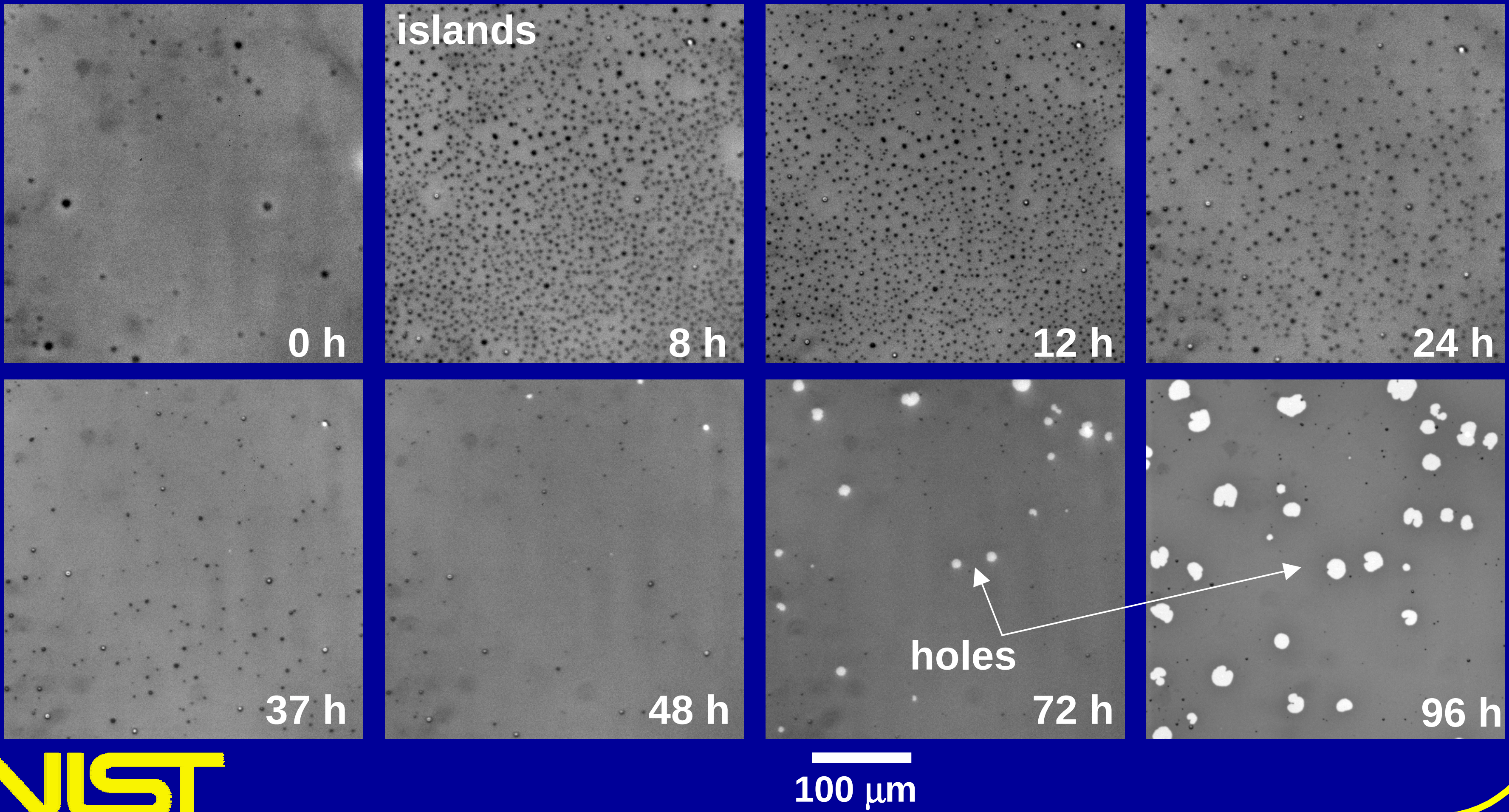
Library Calibration
Kinetics Results

Optical micrographs of block copolymer morphology
target thickness = 69 nm, expect island morphology



Gradient Library Limitation: Gradient "Crosstalk"

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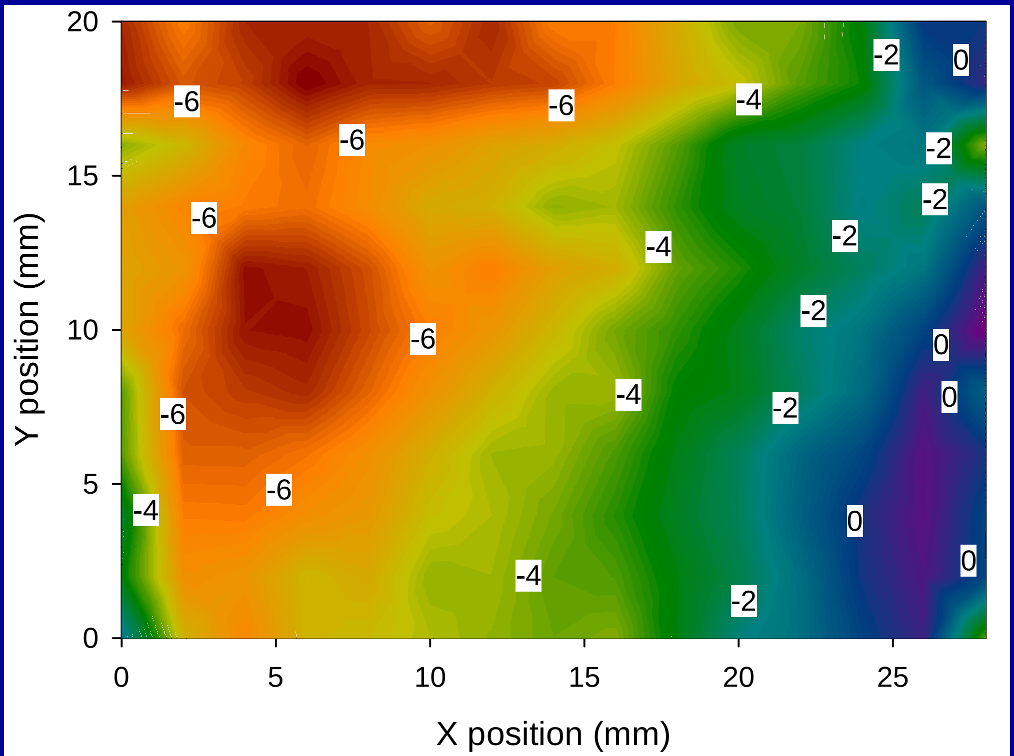
Change in morphology from island to holes indicates change in film thickness due to the temperature gradient

Can use SRG to measure thickness after anneal, thickness change is shown below

175 °C **125 °C**



Sample was annealed 96 h, a relatively long time

This demonstrates how one gradient can modify the second

For the block copolymer kinetics experiment, this crosstalk is fatal

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Conclusions

Demonstrated application of library design and calibration for a actual experimental problem

- Block copolymer thin film ordering
  - Film thickness
  - Surface energy
  - Temperature
  - Time

Emphasized iterative nature of design and calibration steps throughout the experiment

Shown flexibility and limitations of combinatorial technique

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